

Cluster expansion of the wavefunction. Potential energy curves of the ground, excited, and ionized states of Li_2

H. NAKATSUJI,¹ J. USHIO, AND T. YONEZAWA

Division of Molecular Engineering, Graduated School of Engineering, Kyoto University, Kyoto 606, Japan

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This paper is dedicated to Professor Camille Sandorfy on the occasion of his 65th birthday

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The SAC (symmetry-adapted-cluster) and SAC-CI theories based on the cluster expansion of the wavefunction have been applied to the calculations of the potential energy curves of the ground, excited, and ionized states of the Li_2 molecule. The potential energy curves and the spectroscopic properties calculated agree well with the available experimental data and the previous theoretical results of Olson and Konowalow. For the $2^1\Sigma_g^+$ state, our calculation is the first and predicts a bound state whose minimum is at $R_e = 6.8$ bohr and 2.5 eV above the ground state. This state dissociates into 2P and 2S states of the Li atoms and has a hump which is higher than and outside of the hump of the $B^1\Pi_u$ state. The long-range behavior of the states which dissociate into 2P and 2S states of the Li atom is well predicted by the resonance interaction theory.

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On a appliqué les théories SAC et SAC-CI, qui sont basées sur une expansion de l'agglomération de la fonction d'onde, au calcul des courbes d'énergie potentielle des états fondamental, excité et ionisé de la molécule Li_2 . Les courbes d'énergie potentielle et les propriétés spectroscopiques calculées sont en bon accord avec les données expérimentales disponibles ainsi qu'avec les résultats théoriques antérieurs de Olson et Konowalow. Dans le cas de l'état $2^1\Sigma_g^+$, nos calculs correspondent à une première et ils prédisent un état lié dont le minimum se trouverait à $R_e = 6,8$ bohr et à 2,5 eV au-dessus de l'état fondamental. Cet état se dissocie dans les états 2P et 2S de l'atome de Li et il présente un maximum qui est plus élevé que et en dehors du maximum de l'état $B^1\Pi_u$. On peut facilement prédire le comportement à long terme des états qui se dissocient dans les états 2P et 2S de l'atome de Li en faisant appel à la théorie de l'interaction de résonance.

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Introduction

Accurate information on the potential energy hypersurfaces and the electronic structures of molecules, especially those of excited states, are very important for the study of chemical reactions and the dynamic behavior of molecules in excited states. Professor Sandorfy, who has developed various aspects of chemical spectroscopy (1, 2), has accumulated detailed knowledge on excited states, especially those of Rydberg type (3). These activities have, at the same time, increased the need for accurate theoretical data on electronic structures and potential energy hypersurfaces for excited-state molecules.

So far, a practical method of calculating accurate wavefunctions for molecules in excited states in a wide range of molecular configurations has been the CI method applied very carefully by experts. Buenker, Peyerimhoff, and their co-workers (4), for example, have been active in this field. The MC-SCF method has also been applied frequently, though the applicability is rather limited for higher excited states.

Cluster expansions of the wavefunction give another efficient way of calculating accurate correlated wavefunctions for the ground state and the various excited states of molecules (5, 6). We are currently using the Symmetry-Adapted Cluster (SAC) theory (7, 8) for calculations of the lowest closed-shell states, and the SAC-CI theory (8, 9) for calculations of the excited and ionized states generated therefrom. These theories have been successfully applied to the studies of molecular spectroscopy of valence and Rydberg excitations (10, 11) and ionizations of outer and inner valence electrons (11–13). The theory has also been applied to the study of the hyperfine splitting constants of doublet radicals in order to investigate the coupling of spin and electron correlations (14).

For the closed-shell ground state, Bartlett, Purvis, and co-workers (15–17) studied the applicability of the coupled-

cluster theory (18) to the potential curves of N_2 , $\text{Be} + \text{H}_2 \rightarrow \text{BeH}_2$, and the H_2O molecule with the elongated OH distance. They showed the superiority of the coupled-cluster theory in comparison with the CI theory including only single and double excitations from the Hartree–Fock configuration. Their conclusion applies also to the present SAC theory because of the similarity of the two methods. For molecules including multiple bonds, however, an ordinary single-reference coupled-cluster theory fails when the bond length is considerably elongated. There, the multi-reference version of the theory becomes necessary (19–21). Recently, we have developed multi-reference (MR) SAC theory (22). It is exact and unique without imposing completeness on the multi-reference space. It gives accurate descriptions of not only ordinary ground states but also quasi-degenerate states and excited states. This was confirmed from the calculations of the potential energy curves of the ground and excited states of the CO molecule (23).

In this paper, we consider applications of the SAC and SAC-CI theories to calculations of the potential energy curves of the Li_2 molecules in ground, excited, and ionized states. For the Li_2 molecule, the theory is capable of describing the proper dissociation of the ground and lower excited states.

The potential energy curves of the ground state and the lower excited states of Li_2 have been studied extensively by Olson and Konowalow (24) by the MC-SCF method. They studied all the states leading to the lower two separated atom limits, i.e., $^2S + ^2S$ and $^2S + ^2P$, except for the $2^1\Sigma_g^+$ and $2^3\Sigma_u^+$ states. Kutzelnigg *et al.* (25) studied the potential curves of the ground and lowest $^3\Sigma_u^+$ states. Kahn *et al.* (26) studied the $B^1\Pi_u$ potential energy curve. Davies and Jones (27) and Takada *et al.* (28) calculated the lower potential curves by the quasi-degenerate many body perturbation method. Uzer and co-workers (29) analyzed the photodissociation of Li_2 based on the theoretical potential energy curve. Konowalow and Fish (30) recently studied the potential energy curve of the $3^1\Sigma_g^+$ state. We will calculate here the

¹ To whom all correspondence should be addressed.

potential energy curves and the spectroscopic constants of all the states which dissociate into the lower two separated atom limits, $^2S + ^2S$ and $^2P + ^2S$, except for the $2^3\Sigma_u^+$ state. This is the first paper which clarifies the bound nature and the existence of a hump in the $2^1\Sigma_g^+$ state.

For the cation of Li_2 , Henderson *et al.* (31) reported the potential curves of low-lying states at the Hartree–Fock SCF level. Bottcher and Dalgarno (32) reported accurate model potential calculation. Müller and Jungen (33) reported extensive calculations of the potential energy curves. We will study the potential curve of the lowest $2^2\Sigma_g^+$ state.

Method of selecting linked and unlinked operators

The method of calculations in the SAC and SAC-CI theories has already been described in detail (9, 11). The dimension of the matrices to be diagonalized is the same as the number of the linked operators. In the present application, the linked operator includes the identity operator and the single and double excitation operators from the closed-shell Hartree–Fock configurations. The triple and quadruple excitations are considered in the unlinked term. Even in this approximation, the number of linked operators easily becomes large even for moderate basis sets, so that we have adopted a systematic method of selection of linked operators (11). Further, since the calculation of the integrals for the unlinked terms is a time-consuming part, we have also adopted an appropriate method of selecting unlinked terms (11). However, in the calculations of the potential surface, an independent selection of operators for independent geometries may lead to a discontinuity of the potential curve and the properties. Therefore, we have adopted the following method of selections which we call the GSUM method.

An essential point of the GSUM method is to take the group sum of the operators (linked and unlinked) selected for all the representative points in the nuclear configuration space. We first select several representative points in the nuclear configuration space which cover the reaction under consideration. The Hartree–Fock MO's of each geometry are rearranged so as to have the same ordering as the MO's of the adjacent geometries. The linked and unlinked operators are selected for each geometry by the method described in ref. 11. We then take the group sum of these operators and the calculations are carried out at each geometry using the same set of this group sum of operators. This method is appropriate to study continuous changes in the potential energy curves and the properties along the change in nuclear configuration.

Calculational details

The molecular orbitals of Li_2 were calculated by the closed-shell Hartree–Fock–Roothaan method (34), using a slightly modified version of the HONDOG program (35). The HF MO's of the ground state were used as reference MO's for all the ground and excited states studied here. The basis set is (9s5p) GTO's of Huzinaga (36) contracted to (4s2p) set by Dunning (37) augmented with their derivative bases and one *s*-type GTO ($\zeta = 0.01$) as a Rydberg AO. This basis set consists of 74 CGTO's. The derivative bases, which are *p* and *d* GTO's for the *s* and *p* GTO's, respectively, are best suited for describing the polarization of the electron cloud in the course of the reaction as studied previously (38, 39). In the Appendix, we have shown some important effects of these derivative bases on the spectroscopic properties of the ground and lower excited states of Li_2 .

TABLE 1. Dimensions of the linked operators in the SAC and SAC-CI calculations of Li_2

State	Space ^a symmetry	SE ^b	DE ^b	Total
Ground	s	77	234	312
Singlet excited	s	77	579	656
	a	76	562	638
Triplet excited	s	77	627	704
	a	76	707	783
Ionized	s	2	86	88
	a	1	77	78

^as and a denote symmetric and antisymmetric, respectively, with respect to the reflection plane perpendicular to the molecular axis.

^bSE: single excitation, DE: double excitation.

The SAC and SAC-CI calculations were carried out with the program coded by Nakatsuji. As active MO's, we have taken the energetically lowest 54 MO's at the experimental internuclear distance and the corresponding MO's at any internuclear distances. The excitation operators were selected by the method described in ref. 11. The values of the thresholds λ_g and λ_e are 1×10^{-5} au. In the unlinked term, we have included all the double excitation operators whose coefficients are larger than 1×10^{-5} in the SDCl of the ground state. We selected five representative points at 4.0, 5.051, 6.5, 8.0, and 12.0 bohr in the internuclear distances. We have selected the excitation operators at the individual geometries and took the group sum of them by the GSUM method to cover all the reaction path. The dimension of the calculation after the GSUM method is shown in Table 1. They are relatively small by virtue of the cluster expansion theory. The ground state was calculated by the SAC theory and the excited and ionized states were calculated by the SAC-CI theory.

Results

The potential energy curves of the ground and lower excited states of Li_2 are displayed in Fig. 1. We have calculated all the singlet and triplet states of Li_2 which dissociate into the lowest two separated atom limits, $^2S + ^2S$ and $^2P + ^2S$, except for the $2^3\Sigma_u^+$ state. Figure 2 shows the potential energy curves for the lowest ionized states. Table 2 is a summary of the energies of these Li_2 system at various internuclear distances.

We show in Table 3 the spectroscopic constants of all the bound states of Li_2 studied here. The present theoretical values were calculated by the method of Dunham (40) from the potential curves displayed in Fig. 1. The experimental values were cited from Huber and Herzberg (41), Kusch and Hessel (42), and others (43, 44). In cases where the experimental values are not available, we have cited the theoretical values from Olson and Konowalow (24) for Li_2 , and from Müller and Jungen (33) and Henderson *et al.* (31) for Li_2^+ .

For the ground and lower excited states of Li_2 , the general trends and the shapes of the potential energy curves shown in Fig. 1 are very similar to the results of the extensive MC-SCF calculations due to Olson and Konowalow (24). For the $2^1\Sigma_g^+$ state, the present result appears to be the first one reported. It shows an interesting potential curve which will be discussed in more detail later. The quality of the calculated potential curves is judged in detail by a comparison of the spectroscopic constants between theory and experiment (Table 3). For the $X^1\Sigma_g^+$, $A^1\Sigma_g^+$, and $B^1\Pi_u$ states, the adiabatic excitation energy T_e , equi-

TABLE 3. Spectroscopic constants for the ground, excited, and ionized states of Li₂

State	Source	T_e (eV)	R_e (Bohr)	D_e (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α_e (10 ⁻³ cm ⁻¹)	\bar{D}_e (10 ⁻⁶ cm ⁻¹) ^y
$X^1\Sigma_g^+$	Present calc.	0.0	5.097	8258 ^h	343	2.533	0.6605	6.010	9.811
	Exptl. ^b	0.0	5.051	8436 ^d	351	2.610	0.6726	7.04	9.87
$A^1\Sigma_u^+$	Present calc.	1.72	5.938	9161 ^h	250	1.113	0.4868	4.449	7.355
	Exptl. ^b	1.74	5.873	8940 ^d	255	1.58	0.4975	5.40	7.54
$B^1\Pi_u$	Present calc.	2.58	5.630	2241 ^h (3302) ^j	259	4.468	0.5415	11.15	9.470
	Exptl. ^b	2.53	5.546	3102 ^c	270	2.673	0.5577	8.5	9.45
$2^1\Sigma_g^+$	Present calc.	2.52	6.940	2682 ^h (~4708) ^j	164	4.482	0.3564	-9.9785	6.733
$1^1\Pi_g$	Present calc.	2.71	7.504	1184 ^g	139	2.366	0.3047	2.945	5.856
	Previous calc. ^{a,c}	(2.71)	(7.863)	(1297)	(83)	(1.3)			
$a^3\Sigma_u^+$	Present calc.	0.973	7.565	409 ^h	96	3.211	0.2998	11.84	11.62
	Previous calc. ^{a,c}	(0.99)	(8.001)	(292)	(61)	(3.2)			
$1^3\Pi_u^+$	Present calc.	1.39	4.948	11861 ^h	342	2.773	0.7009	4.258	11.78
	Previous calc. ^{a,c}	(1.44)	(4.974)	(11483)	(339)	(2.5)			
$b^3\Sigma_g^+$	Present calc.	2.00	5.862	6913 ^h	244	2.591	0.4994	8.951	8.381
	Previous calc. ^{a,c}	(2.03)	(5.851)	(6811)	(245)	(2.2)			
$2^2\Sigma_g^+$ (Li ₂ ⁺)	Present calc.	5.08	5.918	10341 ^h	255	1.733	0.4900	6.333	7.247
	Previous calc. ^a	5.00	(5.98) ^j	(10160) ^f	(255) ^g	(1.5) ^g			

^a Values in the parentheses are the previous calculated results.

^b Reference 41.

^c Reference 24.

^d Reference 42.

^e Reference 43.

^f Reference 33.

^g Reference 31.

^h Relative to the dissociation limit.

ⁱ Relative to the top of the hump.

^j \bar{D}_e denotes the centrifugal distortion constant, which is entirely different from the binding energy (D_e).

TABLE 4. The hump of the $B^1\Pi_u$ and $2^1\Sigma_g^+$ states of Li_2

Property	$B^1\Pi_u$ state			$2^1\Sigma_g^+$ state, this work
	Theoretical		Exptl.	
	Present	Olson–Konowalow ^a		
Height (cm^{-1})	1056	656	523 ^b , 928 ^c	~2030
Position (bohr)	9.73	10.43	—	~11.6

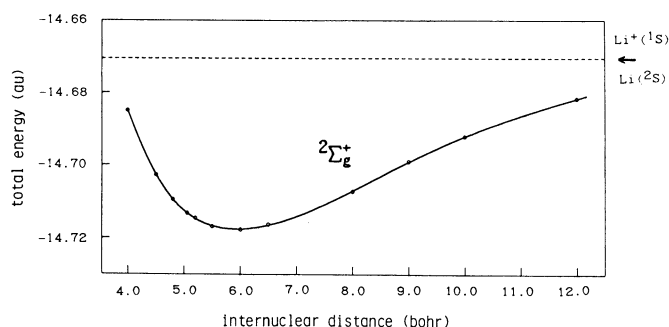
^aReference 24.^bReference 43.^cReference 44.

FIG. 2. Potential energy curves of the lowest ionized states.

shorter bond length region, the potential curves of these states should have a hump somewhere between the valence-type and resonance-type regions. For the $B^1\Pi_u$ state, the hump is at 10.1 bohr and for the $2^1\Sigma_g^+$ state it is at about 11.7 bohr. In Table 4 we have summarized the constants of these humps. Further from this consideration we expect that the shape of the hump is not symmetric with respect to the top position because the nature of the interaction is drastically different between shorter and longer regions. For the $1^3\Pi_g$ state our calculation didn't show any minimum. It is repulsive throughout.

We now discuss each state separately. The ground state, $X^1\Sigma_g^+$ was calculated by the SAC theory. It gives excellent results for the spectroscopic constants and shows a reasonable asymptotic behavior. In the calculation of the excited and ionized states, the electron correlation in this ground state was used as a starting point in the SAC-CI formalism (8, 9).

The $a^3\Sigma_u^+$ state is only very weakly bound, as pointed out by Kutzelnigg *et al.* (25). The calculated equilibrium length is longer than those of Olson and Konowalow. Our potential is more attractive than theirs. However, since the number of sampling points is not enough in the region near the potential minimum, we are not definitive on this conclusion.

The $1^3\Pi_u$ state was interesting due to its relation to the possibility of an alkali-dimer laser. Figure 1 shows that the $1^3\Pi_u$ state potential curve is crossed by the $a^3\Sigma_u^+$ potential curve at its repulsive limb. Therefore the present calculation supports the conclusion of Olson and Konowalow that the Li_2 laser is impossible (24).

The $B^1\Pi_u$ state is an interesting state which has a hump. It is attractive at shorter range because of the valence-type force but repulsive at long range because of the resonance force as shown by eq. [2]. This is the origin of the hump, which is therefore strongly unsymmetric with respect to the position of the hump maximum. From Table 4, the position of the hump maximum is at about 10.1 au. The hump height was calculated

to be 981 cm^{-1} , which is closer to the experimental value of Velasco *et al.* (44). For the valence minimum, both the adiabatic excitation energy T_e and the equilibrium length R_e agree well with experiment (Table 3). The dissociation energy D_e is 2263 cm^{-1} , if it is relative to the dissociation limit. The value in parentheses, 3244 cm^{-1} , is measured relative to the hump maximum. The latter one is closer to the experimental value (43).

The $2^1\Sigma_g^+$ state is reported for the first time in this paper. It is a very interesting state which has a deeper valence-type minimum and higher hump than the $B^1\Pi_u$ state. The origin of the hump is the same as for the $B^1\Pi_u$ state. The maximum position and the height of the hump were analyzed to be 11.7 bohr and 1900 cm^{-1} , respectively, as shown in Table 4. However, since the number of calculated points near the hump is small, these values should be considered to be only semi-quantitative. Near the valence minimum the potential is rather deep but flat. The dissociation energy is 2794 cm^{-1} , if it is measured relative to the dissociation limit, but is about 5300 cm^{-1} relative to the maximum of the hump.

The $3^1\Pi_g$ state is calculated to be repulsive throughout the internuclear distance but has a shoulder between 7.0 and 9.0 bohr as seen from Fig. 1. This feature also corresponds well to the result of Olson and Konowalow. Further, they suggested that an addition of the π - δ configurations to their calculations would lower the potential curve of this state at smaller internuclear distances to produce a local minimum. However, despite the inclusion of the π - δ configurations in our calculation, the present potential curve does not have any local minimum throughout the calculated range.

Lastly, we discuss the $2^2\Sigma_g^+$ state of the Li_2 cation. The calculated potential curve is shown in Fig. 2 and the spectroscopic constants are given at the bottom of Table 3. Because of a loss of an electron from the bonding σ_g orbital, the equilibrium bond length is elongated by about 0.8 au. The potential also becomes flatter near the equilibrium length. However, since the ionization energy of the Li atom, (5.39 eV (48)) is larger than that of the $X^1\Sigma_g^+$ state of Li_2 , (5.00 eV (41)), the dissociation energy of Li_2^+ is larger than that of Li_2 .

Conclusion

The SAC and SAC-CI theories based on the cluster expansion of the wavefunction have been applied to studies of the potential energy curves of the ground, excited, and ionized states of the Li_2 molecule. The calculated potential energy curves and spectroscopic properties agree well with available experimental data and with the previous theoretical results of Olson and Konowalow (24). For the $2^1\Sigma_g^+$ state, the present result is the first calculation. It is an interesting state which has

a deep valence minimum at 6.8 bohr and 2.5 eV above the ground state. It also has a hump of about 1900 cm^{-1} high at about 11.7 bohr. The long-range behavior of the potential curves of the states which dissociate into the $^2P + ^2S$ states of the Li atom are well predicted from the first-order resonance interaction theory (45–47).

For the bond involved in the ground state of the Li_2 molecule, the SAC theory is shown to give an excellent potential curve up to the dissociation limit. The SAC-CI theory is essentially a multi-reference type theory (9) so that it gives a reasonable description of the excited and ionized states. Based on this research, the usefulness of the SAC and SAC-CI theory in the study of molecular excited states and molecular spectroscopy is extended.

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TABLE 5. Comparison of the spectroscopic constants of the ground and lower excited states of Li_2 calculated with and without including the derivative bases

State	Source	T_e (eV)	R_e (au)	D_e (cm^{-1})	ω_e (cm^{-1})
$X^1\Sigma_g^+$	Basis I	0.0	5.165	7682	324
	Basis II	0.0	5.097	8258 ^d	343
	Exptl.	0.0	5.051 ^b	8436 ^c	351 ^b
$A^1\Sigma_u^+$	Basis I	1.62	5.980	9364	258
	Basis II	1.72	5.938	9161 ^d	250
	Exptl.	1.74	5.873 ^b	8940 ^c	255 ^b
$B^1\Pi_u$	Basis I	2.66	5.877	932 ^d (1089) ^e	241
	Basis II	2.58	5.630	2246 ^d (3302) ^e	259
	Exptl.	2.53	5.546 ^b	3102 ^f	270 ^b

^aBasis II includes the derivative basis but Basis I does not.

^bReference 41.

^cReference 42.

^dRelative to the dissociation limit.

^eRelative to the top of the hump.

^fReference 43.

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Appendix

In Table 5 we have shown some spectroscopic properties of the ground and lower excited states of Li_2 calculated with and without including the derivative bases. Basis I is $(3s2p)$ set (49) and Basis II is the basis set used in the text which includes the derivative bases. From Table 5, it is seen that the results calculated with Basis II are consistently superior to those calculated with Basis I. This implies that the role of the derivative functions is important for the calculations of the potential curve.